

ANTHRACENE COMPOUND AND
CHEMILUMINESCENT COMPOSITION COMPRISING THE SAME

BACKGROUND OF THE INVENTION

5

Field of the Invention

10074958-020702
2070207-8567001

10 The present invention relates to an anthracene compound and a chemiluminescent composition comprising the compound, and more particularly to a novel anthracene compound which is capable of emitting a blue light of a high intensity for a prolonged period of time compared with conventional anthracene compounds used as luminescent dyes in chemiluminescent compositions emitting blue light, and a chemiluminescent composition comprising the novel compound.

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Description of the Related Art

One example of known chemiluminescent solutions includes a mixed solution of a chemiluminescent oxalate composition comprising a luminous dye and a solution containing peroxide.

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The chemiluminescent oxalate composition generally contains a luminescent dye, an oxalate and a solvent. The peroxide-containing solution contains peroxide, a catalyst and a solvent.

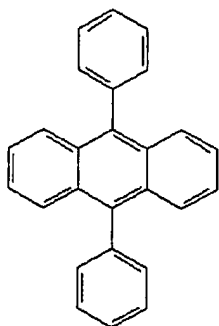
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The color of light generated from the chemiluminescent solution is determined by the luminescent dye used in the

chemiluminescent oxalate composition. As the luminescent dye emitting a blue light, an anthracene compound is known.

As the anthracene compound emitting a blue light, a 9,10-diphenylanthracene compound described in the following formula 1 and a luminescent composition comprising the compound is known.

[Formula 1]



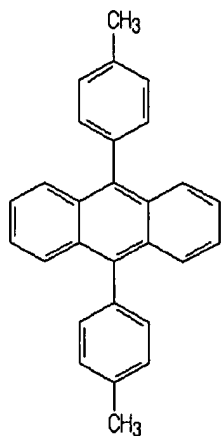
However, there is a disadvantage that the intensity and color of light emitted from the chemiluminescent solution comprising the 9,10-diphenylanthracene compound are rendered unstable with the lapse of time.

Therefore, there have been continuous attempts to find a luminescent dye that stably emits clear blue light. In particular, due to the fact that the physical properties of the 9,10-diphenylanthracene compound change with a substituent applied to the compound, many studies have been investigated.

As one of such studies, U.S. Patent No. 4,678,608 discloses a chemiluminescent composition using a 9,10-bis(4-methylphenyl)anthracene compound represented by the following

formula 2.

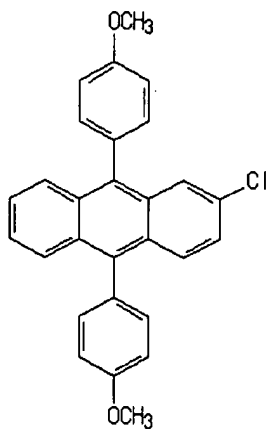
[Formula 2]



However, where the 9,10-bis(4-methylphenyl)anthracene
5 compound is used in the chemiluminescent oxalate composition,
it loses a desired stability. For this reason, the compound
cannot be used in products requiring that luminescence be
maintained for 5 hours or more.

Also, U.S. Patent No. 4,717,511 discloses a
10 chemiluminescent composition using 9,10-bis(4-methoxyphenyl)-2-
chloroanthracene described in the following formula 3

[Formula 3]



However, there is a disadvantage that the 9,10-bis(4-methoxyphenyl)-2-chloroanthracene compound emits pale blue light.

Therefore, the present inventor has endeavored to develop a compound that is capable of emitting a clear blue light for a prolonged period of time, and the present invention has been accomplished by such studies.

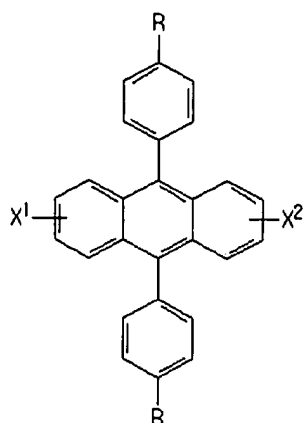
SUMMARY OF THE INVENTION

Therefore, the present invention has been made in view of the above problems, and it is an object of the present invention to provide an anthracene compound which has excellent stability over the conventional luminescent dye emitting blue light, thereby emitting a chemiluminescent light of clear deep blue.

It is another object of the present invention to provide a chemiluminescent composition and a chemiluminescent solution using the anthracene compound.

In accordance with one aspect of the present invention, there is provided an anthracene compound represented by the following formula(4):

[Formula 4]



wherein R is a alkyl group having 1-8 carbon atoms, X^1 and X^2 are independently hydrogen or halogen.

In accordance with another aspect of the present invention, there is provided a preparation method of an anthracene compound comprising:

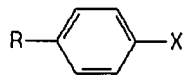
refluxing a compound of the following formula(11) with magnesium metal in an organic solvent and cooling the refluxed solution, thereby affording a compound of the following formula(12);

mixing the obtained compound of the formula(12) and anthraquinone of the following formula(13) in an organic solvent, refluxing the resulting solution adding an aqueous acidic solution, for example, 10% hydrochloric acid solution, extracting an organic phase, and distilling the extracted organic solvent under a vacuum, thereby producing a brown solution of the following formula(14); and

adding acetic acid and a catalyst to the obtained brown solution, and refluxing the resulting solution, thereby

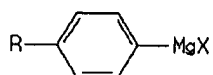
obtaining the solid compound of the formula(4).

[Formula 11]



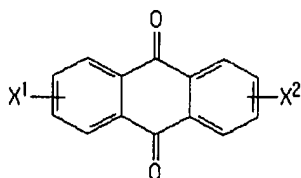
wherein R is an alkyl group having 1-8 carbon atoms, and
5 X is halogen.

[Formula 12]



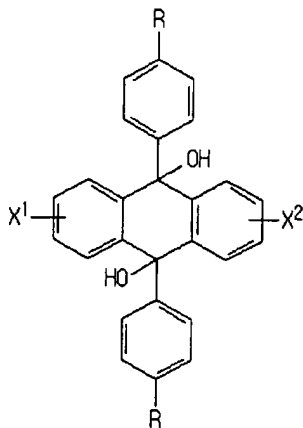
wherein R is an alkyl group having 1-8 carbon atoms, and
10 X is halogen.

[Formula 13]



wherein X¹ and X² are independently hydrogen or halogen.

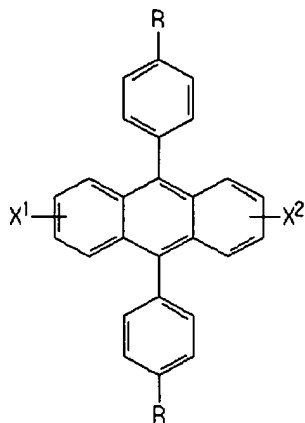
[Formula 14]



15 wherein R is an alkyl group having 1-8 carbon atoms, and

X¹ and X² are independently hydrogen or halogen.

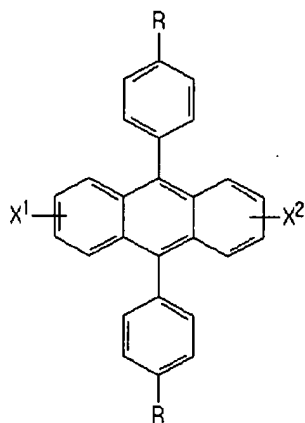
[Formula 4]



wherein R is an alkyl group having 1-8 carbon atoms, and
5 X¹ and X² are independently hydrogen or halogen.

In accordance with another aspect of the present
invention, there is provided a chemiluminescent composition
containing the anthracene compound represented by the
following formula(4):

10 [Formula 4]



wherein R is a alkyl group having 1-8 carbon atoms, X¹
and X² are independently hydrogen or halogen, the

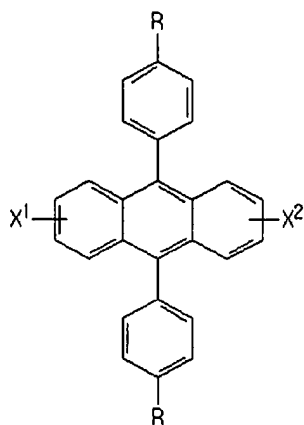
chemiluminescent composition emitting chemiluminescent light
by reaction with peroxide.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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The present invention can be achieved by providing an
anthracene compound represented by the following formula 4:

[Formula 4]



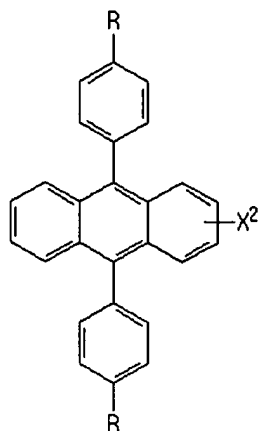
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wherein R is a alkyl group having 1-8 carbon atoms, and
X¹ and X² are independently hydrogen or halogen.

A more preferred compound of the formula 4 is an
anthracene compound represented by the following formula 5, in
which X¹ is hydrogen and X² is halogen:

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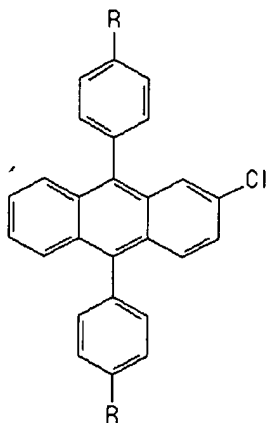
[Formula 5]



wherein R is a alkyl group having 1-8 carbon atoms, and X² is halogen.

A more preferred compound of the formula 5 is an anthracene compound represented by the following formula 6, in which X² is Cl:

[Formula 6]



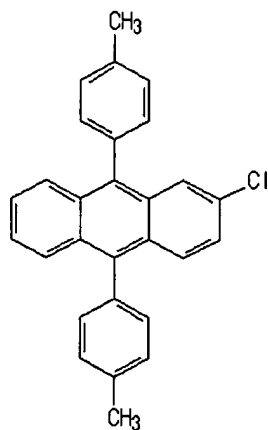
wherein R is a alkyl group having 1-8 carbon atoms.

A more preferred compound of the formula 6 is 9,10-bis(4-methylphenyl)-2-chloroanthracene of the following formula 7, wherein R is a methyl group; 9,10-bis(4-ethylphenyl)-2-chloroanthracene of the following formula 8,

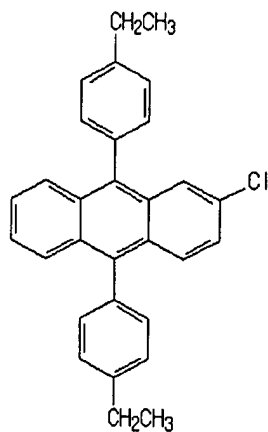
wherein R is a ethyl group; 9,10-bis(4-propylphenyl)-2-chloroanthracene of the following formula 9, wherein R is a propyl group; or 9,10-bis(4-t-butylphenyl)-2-chloroanthracene of the following formula 10, wherein R is a t-butyl group:

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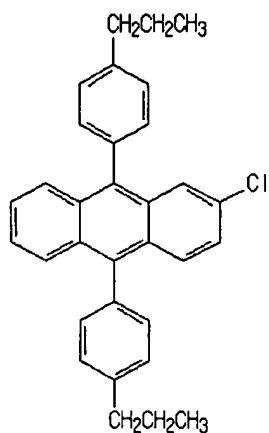
[Formula 7]



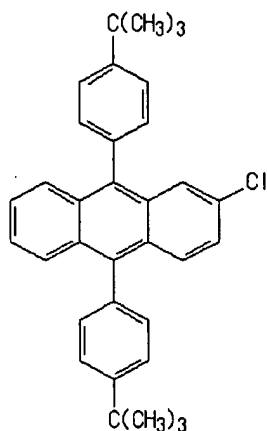
[Formula 8]



[Formula 9]



[Formula 10]



To prepare effectively the anthracene compound of the
 5 formula 4, the present invention provides a preparation method
 comprising the steps of:

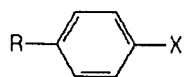
refluxing a compound of the following formula 11 with
 magnesium metal in an organic solvent for 3 hours or more, and
 cooling the refluxed solution, thereby obtaining a compound of
 10 the following formula 12;

stirring the obtained compound of the formula 12 and
 anthraquinone of the following formula 13 in an organic
 solvent for 3 hours or more, refluxing the resulting solution

for 3 hours or more, stirring the resulting solution after
adding an aqueous 10% hydrochloric acid solution, extracting
only the organic solvent, and distilling the extracted organic
solvent under a vacuum, thereby obtaining a brown solution of
the following formula 14; and

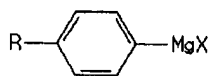
adding acetic acid and a catalyst to the obtained brown
solution, stirring the mixed solution for 1 hour or more,
refluxing the stirred solution for 3 hours or more, stirring
again the refluxed solution for 3 hours or more, and treating
the resulting solution using a recrystallization method,
thereby obtaining the solid compound of the formula 4.

[Formula 11]



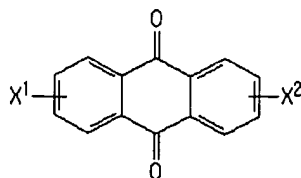
wherein R is an alkyl group having 1-8 carbon atoms, and
X is halogen.

[Formula 12]



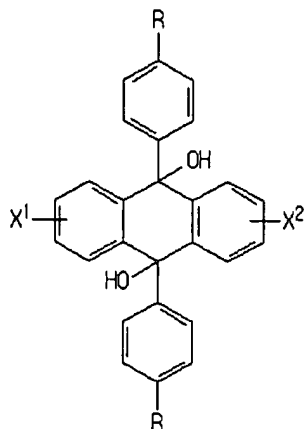
wherein R is an alkyl group having 1-8 carbon atoms, and
X is halogen.

[Formula 13]



wherein X^1 and X^2 is independently hydrogen or halogen.

[Formula 14]



wherein R is an alkyl group having 1-8 carbon atoms, X^1 and X^2 is independently hydrogen or halogen.

As described above, the compound of the formula 11 is refluxed with magnesium metal in the organic solvent for 3 hours or more. The refluxed solution is cooled. In this way, the compound of the formula 12 is obtained.

Various organic solvents can be used in this step. Anhydrous tetrahydrofuran is used as a preferred organic solvent in the present invention. The compound of the formula 11 and magnesium metal are added to the anhydrous tetrahydrofuran solvent at a same equivalent. The resulting solution is refluxed for 3 hours or more and then cooled.

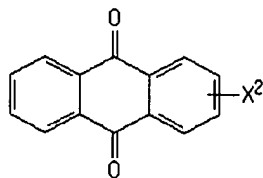
The compound of the formula 11 may be selected from compounds having the structure of the formula 11, wherein X is halogen, and R is an alkyl group having 1-8 carbon atoms, and preferably, wherein X is halogen, and R is methyl, ethyl,

propyl or t-butyl group.

The compound of the formula 12 obtained from the above step and anthraquinone of the formula 13 are stirred in the organic solvent for 3 hours or more. The stirred solution is refluxed for 3 hours or more, and stirred after being added with an aqueous 10% hydrochloric acid solution. An organic solvent is extracted, and the extracted solution is distilled under a vacuum. In this way, the brown solution of the formula 14 is obtained.

A more preferred compound of the formula 13 is an anthracene compound represented by the following formula 15, in which X^1 is hydrogen, and X^2 is halogen:

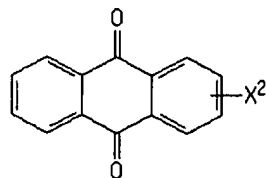
[Formula 15]



wherein X^2 is halogen(F, Cl or Br).

A particularly preferred compound of the formula 15 is an anthracene compound represented by the following formula 16, in which X^1 is hydrogen, and X^2 is halogen:

[Formula 16]



The compound of the formula 12 and anthraquinone of the

formula 13 are added to tetrahydrofuran at the same
equivalent. The mixed solution is stirred for 3 hours or
more, refluxed for 3 hours or more. An aqueous 10%
hydrochloric acid solution is added to the refluxed solution,
5 and stirred. An organic solvent is extracted, and the
extracted organic solvent is distilled under a vacuum, by
which the brown solution of the formula 14 is obtained.

Glacial acetic acid and a reducing agent are added to the
brown solution. The mixed solution was stirred at room
10 temperature for 1 hour or more, and refluxed for 3 hours or
more. The refluxed solution is stirred again for 1 hour or more,
by which the compound of the formula 4 was obtained using a
recrystallization method in glacial acetic acid.

Various kinds of reducing agents can be selected and used
15 as a catalyst, and SnCl_2 is used preferably as the reducing
agent according to the invention.

As described above, glacial acetic acid and a reducing
agent are added to the brown solution of the formula 14. The
mixed solution is stirred at room temperature for 1 hour or
20 more, refluxed for 3 hours or more, and stirred again at room
temperature for 1 hour or more. The resulting solution is
subject to a conventional recrystallization method, by which
the anthracene compound of the formula 4 is obtained in the
form of solid.

The anthracene compound represented by the above The formula 4 emits light of blue series having wavelengths of 400nm to 500nm under prescribed conditions for obtaining chemiluminescence using conventional anthracene compounds. The anthracene compound can also generate variously colored light by proper mixing with other fluorescent dyes. Accordingly, the anthracene compound of the formula 4 according to the invention can be used as a fluorescent dye in compositions for emitting chemiluminescence light, similar to the conventional anthracene compounds.

Accordingly, the present invention provides a chemiluminescent composition comprising the anthracene compound of the formula 4, capable of generating chemiluminescence by reaction with peroxide.

Preferably, the anthracene compound of the formula 4 is present in the composition according to the present invention in an amount of 0.1 to 1.0 parts by weight, based on 100 parts by weight of the composition. Where the anthracene compound is present in an amount of less than 0.1% by weight, there is a problem that the generated light is poor in intensity and duration. Where the anthracene compound is present in an amount of more than 1.0%, the anthracene compound may be precipitated in the form of solid. Accordingly, it is preferable that the anthracene compound is contained in the prescribed range. More preferably, the anthracene compound is present in the

composition in an amount of, 0.15 to 0.5 parts by weight, based on 100 parts by weight of the composition.

More preferably, the anthracene compound of the formula 4 is selected from the group consisting of 9,10-bis(4-methylphenyl)-2-chloroanthracene, 9,10-bis(4-ethylphenyl)-2-chloroanthracene, 9,10-bis(4-propylphenyl)-2-chloroanthracene and 9,10-bis(4-t-butylphenyl)-2-chloroanthracene.

The chemiluminescent composition comprising the anthracene compound of the formula 4 also comprises a solvent.

According to the present invention, the solvent may be selected from the group consisting of tertiary alcohols, dibutyl phthalate, butyl benzoate and the mixtures thereof.

The chemiluminescent composition according to the present invention also contains an oxalate compound. Preferably, bis(2,4,5-trichloro-6-carbopentoxypheyl)oxalate may be used as the oxalate compound.

According to the invention, the oxalate compound is present in the composition in an amount of 5 to 18 parts by weight, based on 100 parts by weight of the composition. Where the oxalate compound is present in an amount of less than 5.0 parts by weight, based on 100 parts by weight of the composition, the intensity of light will be very weak. Where the oxalate compound present in an amount of more than 18%, there will be a problem in that the oxalate compound is precipitated in the form of solid. Accordingly, it is

Figure 1. The 12 test items of the TAP. The items are arranged in a vertical column, showing various patterns of black and white squares and lines, representing different test stimuli.

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contains peroxide in an amount of 0.5 to 5parts by weight,
based on 100 parts by weight of the solution. Where peroxide is
present in the solution in an amount of less than 0.5 parts by
weight, based on 100 parts by weight of the solution, the
5 initial chemiluminescence will be weak. Where peroxide is
present in an amount of more than 5%, the intensity of initial
chemiluminescent light is so high that the duration of
chemiluminescence is shorter. Accordingly, it is preferable
that peroxide is present in the prescribed range. The peroxide-
10 containing solution more preferably contains peroxide in an
amount of 1 to 3 parts by weight, based on 100 parts by weight
of the solution. Peroxide may be hydrogen peroxide or peroxides
of carboxylic acid and the like, but is preferably hydrogen
peroxide in view of reactivity.

15 The peroxide-containing solution also contains a solvent.
According to the present invention, the solvent is selected
from the group consisting of tertiary alcohol, dimethyl
phthalate, dibutyl phthalate, butyl benzoate and the mixtures
thereof.

20 Further, the peroxide-containing solution contains a
catalyst. In the present invention, salicylate is preferably
used as the catalyst. The catalyst is preferably present in the
solution in an amount of 0.003 to 0.03 parts by weight, based
on 100 parts by weight of the solution.

25 When the peroxide-containing solution having the above

composition is mixed with the chemiluminescent composition of the present invention in the prescribed ratio, deep blue chemiluminescence lasts for 5 to 48 hours or more, and afterglow lasts for 60 hours or more.

5 The chemiluminescent light generated by the present composition can be used in common application fields, for example, for signaling, decoration, games, hunting, fishing or military purposes.

10 Now, examples of the present invention will be described in more detail. The following examples are described only for a better understanding of the present invention, and are not intended to limit the invention.

Synthetic Example 1

15 Synthesis of 9,10-bis(4-methylphenyl)-2-chloroanthracene
213.8g of 4-bromotoluene dissolved in anhydrous THF(200ml) was slowly added to 32.6g of magnesium in 500ml of anhydrous THF for 2 hours. The mixed solution was refluxed for 3 hours, and then cooled to room temperature. 121g of 2-chloroanthraquinone was added to cooled solution. The
20 resulting solution was stirred for 3 hours, and then refluxed for 3 hours. Then, 400ml of 10% aqueous hydrochloric acid solution was added to the resulting solution. An organic layer was separated from the solution. The resulting solvent
25 was distilled under a vacuum, by which a brown solution was

obtained. 500ml of Glacial acetic acid and 100g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were added to the brown solution. The mixed solution was stirred at room temperature for 1 hour, heated for 3 hours and refluxed. The solution was further stirred at room temperature for 3 hours. Thus, a pale yellow product was obtained. This product was recrystallized using glacial acetic acid. In this way, a pure product was obtained in the form of pale yellow crystals(153g, m.p. 202-203.5°C, yield 78%). Results of ^1H NMR(200MHz, CDCl_3) and IR(KBr) for the obtained compound are described in the following Table 1.

Synthetic Example 2

Synthesis of 9,10-bis(4-ethylphenyl)-2-chloroanthracene

The procedure of Synthetic Example 1 was repeated using 231g of p-bromoethylbenzene instead of p-bromotoluene. In this way, a product was obtained in the form of pale yellow crystals(160g, m.p. 214.5-216.3°C, yield 76%). Results of ^1H NMR(200MHz, CDCl_3) and IR(KBr) for the obtained compound are described in the following Table 1.

Synthetic Example 3

Synthesis of 9,10-bis(4-propylphenyl)-2-chloroanthracene

The procedure of Synthetic Example 1 was repeated using 249g of p-bromopropylbenzene instead of p-bromotoluene. In this way, a product was obtained in the form of pale yellow

crystals(175g, m.p. 225-227°C, yield 78%). Results of ¹H NMR(200MHz, CDCl₃) and IR(KBr) for the obtained compound are described in the following Table 1.

5 Synthetic Example 4

Synthesis of 9,10-bis(4-butylphenyl)-2-chloroanthracene

The procedure of Synthetic Example 1 was repeated using p-bromo-t-butylbenzene(266.4g) instead of p-bromotoluene. In this way, a product was obtained in the form of pale yellow crystals(190.8g, dec > 350°C, yield 80%). Results of ¹H NMR(200MHz, CDCl₃) and IR(KBr) for the obtained compound are summarized in the following Table 1.

Table 1

Examples	¹ H NMR(200MHz, CDCl ₃)	IR(cm ⁻¹)
Syn. Ex. 1	δ 2.53(s, 6H), δ 7.2-7.8(m, 15H)	2916, 1602, 1513, 1441, 1392
Syn. Ex. 2	δ 1.40(t, 6H), δ 2.82(q, 4H), δ 7.2-7.8(m, 15H)	2962, 1601, 1513, 1439, 1391
Syn. Ex. 3	δ 1.42(t, 6H), δ 1.70(m, 4H), δ 2.85(t, 4H), δ 7.2-7.8(m, 15H)	2963, 1602, 1513, 1440, 1391
Syn. Ex. 4	δ 3.91(s, 18H), δ 7.2-7.8(m, 15H)	2957, 1602, 1441, 1390

Based on Table 1, it is seen that the anthracene compounds obtained from Synthetic Examples 1, 2, 3 and 4 are 9,10-bis(4-methylphenyl)-2-chloroanthracene, 9,10-bis(4-ethylphenyl)-2-chloroanthracene, 9,10-bis(4-propylphenyl)-2-chloroanthracene and 9,10-bis(4-t-butylphenyl)-2-

chloroanthracene respectively.

Preparation Example 1 of Chemiluminescent Composition

13.5g of bis(2,4,5-trichloro-6-
5 carbopentoxyphenyl)oxalate was added to a vessel containing
86.25g of dibutyl phthalate. The mixed solution was heated to
120°C and cooled to 60°C under nitrogen atmosphere while being
stirred. Then, 0.250g of 9,10-bis(4-methylphenyl)-2-
chloroanthracene obtained from the Synthetic Example 1 was
10 added the solution. The resulting solution was stirred
thoroughly, and then cooled to room temperature, by which a
chemiluminescent composition was obtained.

Preparation Example 2 of Chemiluminescent Composition

15 The procedure of Preparation Example 1 was repeated
using an equivalent molar amount of 9,10-bis(4-ethylphenyl)-2-
chloroanthracene(0.268g) obtained from Synthetic Example 2
instead of 9,10-bis(4-methylphenyl)-2-chloroanthracene
obtained by Synthetic Example 1, by which a chemiluminescent
20 composition was obtained.

Preparation Example 3 of Chemiluminescent Composition

The procedure of Preparation Example 1 was repeated
using an equivalent molar amount of 9,10-bis(4-propylphenyl)-
25 2-chloroanthracene(0.286g) obtained from Synthetic Example 3

instead of 9,10-bis(4-methylphenyl)-2-chloroanthracene
obtained by Synthetic Example 1, by which a chemiluminescent
composition was obtained.

5 Preparation Example 4 of Chemiluminescent Composition

10 The procedure of Preparation Example 1 was repeated
using an equivalent molar amount of 9,10-bis(4-t-butylphenyl)-
2-chloroanthracene(0.10g) obtained from Synthetic Example 4
instead of 9,10-bis(4-methylphenyl)-2-chloroanthracene
obtained by Synthetic Example 1 due to solubility, by which a
chemiluminescent composition was obtained.

 Comparative Preparation Example 1 of Chemiluminescent
Composition

15 The procedure of Preparation Example 1 was repeated
using an equivalent molar amount of known 9,10-bis(4-
methoxyphenyl)-2-chloroanthracene(0.270g) instead of 9,10-
bis(4-methylphenyl)-2-chloroanthracene obtained by Synthetic
Example 1, by which a chemiluminescent composition was
20 obtained.

 Comparative Preparation Example 2 of Chemiluminescent
Composition

25 The procedure of Preparation Example 1 was repeated
using equivalent molar amounts of known 9,10-bis(4-

methylphenyl)anthracene(0.228g) instead of 9,10-bis(4-methylphenyl)-2-chloroanthracene obtained by Synthetic Example 1, by which a chemiluminescent composition was obtained.

5 Preparation Example 1 to 4 of Chemiluminescent Solution

4.0g of Hydrogen peroxide and 0.018g of salicylate were added to 96g of a mixed solution of dimethyl phthalate and t-butanol(8:2). The obtained solution was mixed with each of the compositions obtained from Preparation Examples 1 to 4 in the ratio of 1:3 to a total weight of 4.0g, by which chemiluminescent solutions were obtained. Then, the intensity of light was measured at intervals by a powermeter(from Coherent Co.; Model No. : FM) while all outside light was excluded in a box of 28cm×25cm×13cm in size. The results are summarized in the following Table 2.

Table 2

Examples	Light intensity (nW) according to time(hr)										
	0.5	1	2	3	4	6	8	10	12	24	Av.
Ex. 1	230	148	84	65	41	25	14	13	9	4	57.63
Ex. 2	240	154	96	75	50	30	19	15	9	5	63.18
Ex. 3	249	159	106	84	62	38	25	18	12	7	69.36
Ex. 4	197	132	76	54	37	21	11	9	7	4	50.18
Com. Ex. 1	257	148	87	62	35	19	10	6	4	0	57.18
Com. Ex. 2	130	65	35	25	16	15	9	5	3	0	27.72

20 As shown in Table 2, it was found that 1 hour after initial light emission, chemiluminescent solutions of Examples 1 to 4 according to the present invention emitted a light of

high intensity for a prolonged period of time, as compared with Comparative Examples 1 and 2. Also, chemiluminescent solutions of Examples 1 to 4 exhibit superior afterglow characteristics over Comparative Examples 1 and 2. Although results of 24 hours later are not shown in Table 2, afterglow could be macroscopically observed from Examples 1 to 4, the chemiluminescent solutions according to the present invention, even after 48 hours.

As described above, the present invention provides a chemiluminescent composition, which has excellent stability compared with conventional chemiluminescent compositions generating blue light, and which has strong initial light intensity and long afterglow duration. The present invention also provides a chemiluminescent solution based on the chemiluminescent composition.